

# Electrochemical De-intercalation, Oxygen Non-stoichiometry, and Crystal Growth of $\text{Na}_x\text{CoO}_{2-\delta}$

F. C. Chou<sup>1</sup>, E. T. Abel<sup>1,2</sup>, J. H. Cho<sup>2,\*</sup> and Y. S. Lee<sup>1,2</sup>

<sup>1</sup>Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139 and

<sup>2</sup>Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139

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We report a detailed study of de-intercalation of Na from the compound  $\text{Na}_x\text{CoO}_{2-\delta}$  using an electrochemical technique. We find evidence for stable phases with Na contents near the fractions  $x \simeq 1/3$ ,  $1/2$ ,  $5/8$ ,  $2/3$ , and  $3/4$ . Details regarding the floating-zone crystal growth of  $\text{Na}_{0.75}\text{CoO}_2$  single crystals as well as results from magnetic susceptibility measurements. We observe the presence of significant oxygen deficiencies in powder samples of  $\text{Na}_{0.75}\text{CoO}_{2-\delta}$  prepared in air, but not in single crystal samples prepared in an oxygen atmosphere. The oxygen deficiencies in a  $\text{Na}_{0.75}\text{CoO}_{2-\delta}$  sample with  $\delta \sim 0.08$  remain even after electrochemically de-intercalating to  $\text{Na}_{0.3}\text{CoO}_{2-\delta}$ .

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## I. INTRODUCTION

Following the discovery of  $\text{Li}_x\text{CoO}_2$  as a good cathode material for use in solid state batteries,<sup>1</sup> the  $\text{Na}_x\text{CoO}_2$  compound was also identified as a candidate having high energy density with good reversibility.<sup>2</sup> Further research on  $\text{Na}_x\text{CoO}_2$  was spurred by the observation of its large thermoelectric power.<sup>3</sup> The discovery of superconductivity in hydrated  $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  with  $T_c \sim 4.5$  K has led to much recent interest in this material.<sup>4</sup> There is the intriguing possibility that strong electronic correlations play an important role in the superconductivity. For further experimental work, high quality single crystals with precisely controlled Na contents are greatly desired. The traditional flux method of crystal growth, using NaCl as a flux, typically yields very thin crystals of limited size.<sup>5</sup> Recently, several groups have reported growing large crystals of  $\text{Na}_x\text{CoO}_2$  using the optical floating-zone technique with a stoichiometric self flux.<sup>6,7,8,9</sup> For these crystals, different methods have been used to control the Na content  $x$ , and the reported measurements of the physical properties show a larger degree of variability compared with measurements on powder samples.

Chemical de-intercalation using  $\text{Br}_2$  has been widely utilized to de-intercalate Na ions from  $\text{Na}_x\text{CoO}_2$ . By adjusting the Br concentration of the solution, various phases with different  $x$  can be obtained.<sup>10</sup> We have developed an electrochemical technique for de-intercalating Na. The sample is immersed, along with a counter electrode and a reference electrode, in a solution of NaOH. By applying a voltage between the sample and counter electrode, an electrochemical double layer ( $\sim 10\text{\AA}$  in thickness) forms at the sample's surface. The high gradient of reactant together with the applied over-potential induces the desired chemical reaction. Using this method, we can monitor the integrated charge during the de-intercalation process. Moreover, the charging rate for the sample can be readily controlled, and thus it may be easier to achieve equilibrium phases. Using this

electrochemical technique, we have employed a potential step method to extract information on the stable phases of  $\text{Na}_x\text{CoO}_2$ .

The possibility of oxygen deficiency in  $\text{Na}_x\text{CoO}_2$  is an important issue, especially in determining the valence of the Co ions. Significant oxygen deficiency is generated in the related  $\text{Li}_x\text{CoO}_{2-\delta}$  system when  $x$  is below  $\sim 0.5$ ,<sup>11</sup> which prohibits further changes to the valence of Co above  $+3.5$ . The instability of the  $\text{Co}^{4+}$  valence state may also make  $\text{Na}_x\text{CoO}_2$  prone to be oxygen deficient, especially for  $x$  below  $\sim 0.5$ . In an earlier study, Molenda *et al.* found that  $\text{Na}_{0.7}\text{CoO}_{2-\delta}$  prepared with an oxygen partial pressure of  $\sim 0.2$  atm had an oxygen defect level as high as  $0.073$ .<sup>12</sup> The degree of oxygen deficiency will likely depend strongly on the method of sample preparation. We have investigated the presence of such deficiencies in both powder and single crystal samples. In addition, we have measured how the de-intercalation process affects the deficiency level. Clearly, if oxygen deficiencies exist, they would strongly affect the electronic structure of the  $\text{CoO}_2$  planes.

This paper is organized as follows: Section II discusses the sample preparation and measurement methods used. Our results, which are intimately connected to our sample preparation methods, are also presented in this section. These results include data from thermal gravimetric analysis, x-ray diffraction, magnetic susceptibility experiments, and measurements of the integrated charge passed through the electrochemical cell. Section III contains a discussion and conclusions.

## II. EXPERIMENTAL DETAILS AND RESULTS

The single crystals used in this study were grown using the travelling-solvent floating-zone (FZ) technique with a stoichiometric self-flux. The feed rod was melted and re-crystallized using a CSI four-mirror furnace with Xe-lamps under various pulling rates.<sup>8</sup> Samples with vari-

ous Na contents were prepared by electrochemically de-intercalating an as-grown  $\text{Na}_{0.75}\text{CoO}_2$  crystal. The basic set up for the electrochemical cell was described in our previous work.<sup>8</sup> Crystals with  $x = 0.67, 0.5$  and  $0.3$  were prepared by ramping the applied voltage in small steps ( $0.001$  mV/step) from the initial open circuit potential to final constant potentials of  $\sim 0$  V,  $0.3$  V, and  $0.7$  V (relative to a Ag/AgCl reference) respectively. The samples were determined to have a single structural phase with the expected c-axis lattice constant reported in the literature by x-ray diffraction, and the Na content was determined by electron probe microanalysis (EPMA). The magnetic properties were characterized using a SQUID magnetometer (Quantum Design MPMS-XL) with an applied field of  $100$  Oe and  $1$  Tesla. The oxygen and water contents were calculated from the weight loss/gain of samples in an oxygen atmosphere using thermal gravimetric analysis (Perkin-Elmer TGA7), and the melting points were checked by differential thermal analysis (Perkin-Elmer DTA7).

### 1. Floating zone crystal growth and characterization

In order to test whether a direct re-crystallization process is suitable for the crystal growth of  $\text{Na}_{0.75}\text{CoO}_2$ , differential thermal analysis (DTA) measurements on stoichiometric  $\text{Na}_{0.75}\text{CoO}_2$  powder were performed. The results are shown in Fig. 1. The sample melts incongruently near  $\sim 1020^\circ\text{C}$  and subsequently enters a completely liquid phase near  $\sim 1075^\circ\text{C}$ . The  $1020^\circ\text{C}$  peak is observed to have a doublet structure which suggests that the incongruent melting process crosses two tie lines upon heating, each associated with a solid phase of different stoichiometry. It is possible that the solidification process during the crystal growth may only quench one of the solid phases. Since the temperature difference between these two solid phases is small ( $\sim 15 - 20^\circ\text{C}$ ), a mixture of two solid phases is very likely. As a result, large single-phase crystals are difficult to produce. This difficulty is exacerbated by the conditions of continuous Na loss during the growth. These difficulties may underlie the discrepancies between powder and FZ crystal measurements, and even between measurements performed on FZ crystals grown by slightly different procedures.<sup>7,9,13,14</sup>

To address Na vapor loss, a rapid-heating technique has been developed for powder preparation and has proven to be reliable in obtaining single phase samples between  $x = 0.65$  and  $0.75$ .<sup>15</sup> This minimizes the amount of a possible CoO impurity phase. The presence of a CoO impurity phase can be detected by comparing DTA scans of  $\text{Co}_3\text{O}_4$  (not shown) and powder  $\text{Na}_{0.75}\text{CoO}_2$ . As shown in Fig. 1, the powder  $\text{Na}_{0.75}\text{CoO}_2$  shows a pronounced solidification exothermic peak  $\sim 860^\circ\text{C}$ , which corresponds to the CoO phase formation. On the other hand, the single crystal lacks significant signature of a CoO impurity phase. The CoO phase does not necessarily become solidified in the crystal if Na loss is constantly

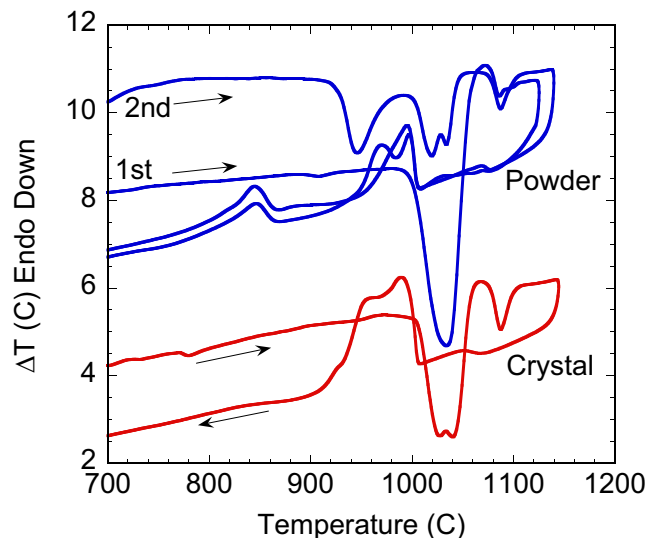


FIG. 1: (color online) DTA scan for  $\text{Na}_{0.75}\text{CoO}_2$  powder and FZ crystal. The scan has been done with warming/cooling rate of  $40^\circ\text{C}/\text{min}$  in an oxygen environment.

compensated. Since it is difficult to maintain a constant flux ratio, it is preferable to fix the heating power and adjust the feeding rate of the stoichiometric feed rod in order to maintain a stable molten zone.

We find that the FZ crystals have a morphology which depends significantly on the pulling rate. The c-axis is always perpendicular to the growth direction and the crystal is relatively easy to cleave along the ab plane. A slow pulling rate below  $2$  mm/h yields crystals with many misaligned grains, independent of the quality of the seed. The misaligned grains of  $1-3$  mm size are hard to cleave, and the grain boundaries contain a CoO impurity phase. On the other hand, fast pulling rates (higher than  $8$  mm/h) can usually prevent misalignment along the growth direction and yield large rod-shaped single crystals. The crystals grown via fast pulling are easy to cleave into large flat pieces. For this pulling rate, a low level of CoO impurity inclusion can be achieved with proper adjustment of extra feed to maintain a stable molten zone, i.e. when the correct flux ratio is obtained so that solid phase  $\text{Na}_{0.75}\text{CoO}_2$  precipitates from the flux continuously.

The visual appearance of the surface of the crystalline rod is not a reliable indicator of overall crystal quality. Crystals grown with an intermediate pulling rate of  $4$  mm/hr have an outer surface with a mirror-like finish, however the core region of the rod is composed of small misaligned domains. There appears to be a high level of CoO impurity phase within the grain boundaries inside the core region. EPMA results indicate the Na content to be near  $0.75$  to within the experimental error ( $\pm 0.08$  from different batches and regions) and there is no significant difference of the Na concentration between the core and outer ring regions of the crystalline rod.

In much of the literature there are subtle discrepancies between magnetic susceptibility measurement performed on FZ single crystals of  $\text{Na}_x\text{CoO}_2$  ( $x > 0.65$ ) grown by slightly different methods. The primary discrepancies regard the magnitude of the susceptibility and the presence of a broad feature near 290 K. We mechanically separated the core material from the outer shiny material from our crystal grown at the 4mm/hr pulling rate. We then measured both materials separately in a SQUID magnetometer. The top panel of figure 2 shows the susceptibility of the core region. Since CoO has an anti-ferromagnetic transition near 290 K, it is reasonable to assume that the broad feature near 290K is due to the presence of a CoO impurity phase. After subtracting a 7 wt% CoO contribution, the magnitude and shape of the curves better agree with measured powders. The bottom panel of Fig. 2 shows the susceptibility measured on the shiny outer region along the c- and ab-directions. When a powder average is taken of the two directions, a curve strongly resembling the powder susceptibility is recovered. Hence, the shiny outer regions of the as-grown crystal are largely free of CoO impurities. These data also illustrate that the magnetic susceptibility is quite sensitive to CoO content; even if no CoO was detected using x-ray diffraction, it may be noticeable in the susceptibility.

## 2. Electrochemical de-intercalation

The electrochemical cell was prepared as described previously,<sup>8</sup> with  $\text{Na}_{0.75}\text{CoO}_{1.92}$  powder as the working electrode, platinum as the anode, Ag/AgCl as the reference electrode, and 1M NaOH as the electrolyte. We have employed a potential step method to extract phase information on  $\text{Na}_x\text{CoO}_2$ , similar to that used previously to study  $\text{La}_2\text{NiO}_{4+\delta}$  and related compounds.<sup>16</sup> In the potential step method, the over-potential at the sample is incremented in small steps. After each step, the potential is held constant for a sufficiently long time such that the current decays to a nearly constant background level, indicating that equilibrium is nearly achieved. Hence, the reference potential measured for the cell can be related to the chemical potential of Na in the sample. Since extremely long times may be required to achieve equilibrium, in practice the voltage is held constant until the current falls below a threshold value. At this point, the next voltage increment is added. This procedure ensures consistent charge dynamics at each new voltage.

In our experiments, the voltage was stepped from the initial open circuit potential of about -0.15 V to 0.6 V in 5 mV steps (measured in reference to Ag/AgCl). After each voltage step, the current through the electrolyte was allowed to decay to 0.25 of the initial current. The current was then extrapolated to infinite charging time assuming exponential decay, and then integrated to obtain  $dq$  for each new voltage increment (where  $dq$  is the extrapolated charge which passes through the electrodes

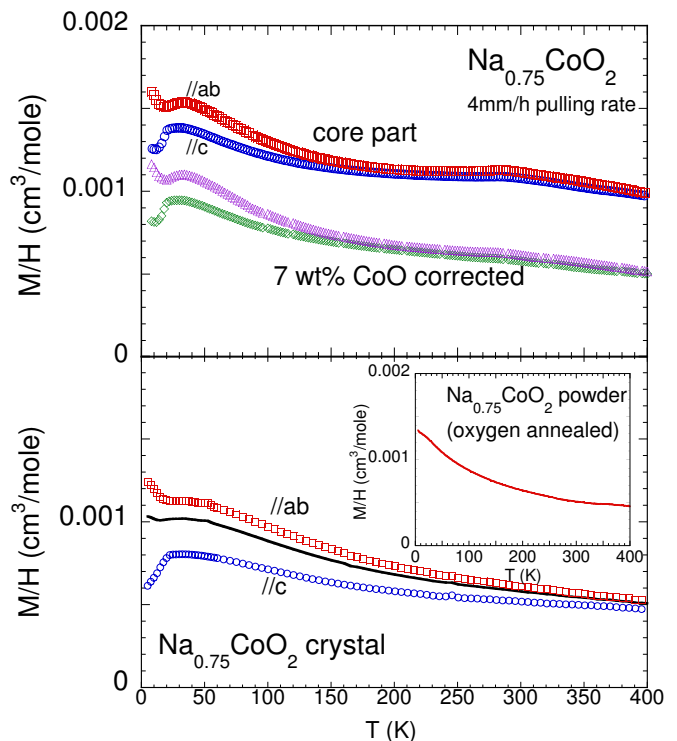
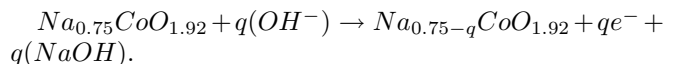


FIG. 2: (color online) Magnetic susceptibilities of a floating zone  $\text{Na}_{0.75}\text{CoO}_2$  crystal, which has been grown with 4 mm/hr pulling rate. The upper panel shows data from the core part, with and without  $\sim 7$  wt% CoO correction. The lower panel is the outer ring part without 290K peak and the solid line corresponds to its powder average. Inset shows measurement for a powder sample with  $x = 0.75$

as equilibrium is approached). The total accumulated charge for all voltage steps,  $q$ , (in electrons per formula unit of  $\text{NaCoO}_2$ ) is plotted for each value of the applied voltage  $V$ , as shown in Fig. 3. Also in the figure, we plot  $dq'/dV$ , where  $dV$  is the 5 mV voltage increment and  $dq'$  is the actual integrated charge during the time the voltage was held constant. (Hence,  $dq'/dV$  is qualitatively similar to  $dq/dV$ , except the magnitude is smaller.) The plateau regions (where  $V$  is roughly constant for a range of  $q$ ) indicate the coexistence of two phases. Thus, the high- $q$  side of each plateau region indicates a Na content corresponding to a single stable phase. The voltages at which these stable phases occur are marked by the peaks in  $dq'/dV$ .

The proposed half reaction at the working electrode is



Since the initial powder sample is  $x = 0.75$ , we can identify stable phases with  $x \simeq 2/3$ ,  $5/8$ ,  $1/2$ , and  $1/3$  near the end of each plateau region. We note that the two plateau regions between  $x \sim 5/8$  and  $1/2$  suggest that there are two narrowly separated phases of close stoi-

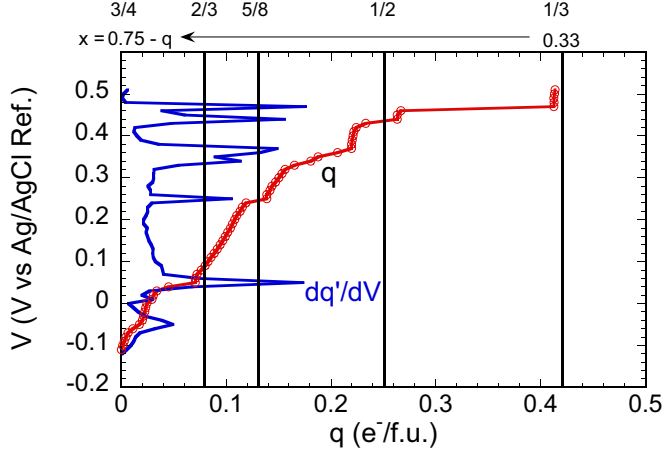


FIG. 3: (color online) Applied voltage versus accumulated charge which passed through the electrochemical cell, where powder sample of  $x = 0.75$  is used as working electrode.

chemistry (within  $\sim 0.02$ ) for this Na content. In addition, the chemical potential difference between  $x = 1/2$  and  $1/3$  is extremely small and this two-phase region is the widest among the observed stable phases. The close proximity of the chemical potential between the phases with  $x = 1/2$  and  $x = 1/3$  indicates that they are close in free energy, and thus may have similar physical properties. This is consistent with the observation that the susceptibilities and Co Knight shift data above  $\sim 100\text{K}$  for both phases are quite similar.<sup>10,17,18</sup>

Fig. 4 shows the results of an ex-situ x-ray diffraction measurements on samples prepared with various applied electrochemical potentials. Using  $\text{Na}_{0.75}\text{CoO}_2$  powder as the starting material, we applied a potential which was ramped from the initial open circuit potential to a final value at a rate of  $0.001\text{ mV/s}$ . The voltage was then held at the final potential for 24 hours, after which the sample was removed from the cell and immediately placed into the x-ray diffractometer. The samples corresponding to the end points at  $0.7\text{V}$  and  $-1.2\text{V}$  were allowed to equilibrate for one week and one month respectively to ensure total conversion. We find that the c-axis lattice constant increases from  $\sim 10.8\text{ \AA}$  to  $\sim 11.2\text{ \AA}$  with increasing potential, which agrees fairly well with the results on Br de-intercalated samples for  $x = 0.75$  and  $x = 0.3$  respectively.<sup>10</sup> Samples prepared with a negative over-potential ( $< -0.5\text{V}$ ) will have Na ions intercalated back into the starting compound  $\text{Na}_{0.75}\text{CoO}_2$ . Hence, phases with higher  $x$  can be formed, and it appears that one such phase has a stoichiometry with  $x$  near  $5/6$ .

### 3. Oxygen non-stoichiometry

It has been reported that significant oxygen deficiencies are generated in the related  $\text{Li}_x\text{CoO}_{2-\delta}$  compound when  $x$  is below  $\sim 0.5$ ,<sup>11</sup> impeding higher valence changes

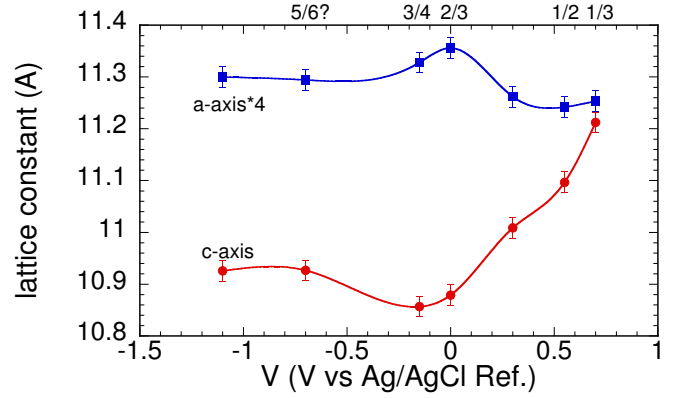


FIG. 4: (color online) Ex-situ x-ray diffraction c-axis versus applied voltage. The applied voltage has been ramped up ( $0.001\text{ mV/s}$ ) from the initial open circuit potential to the final equilibrium potential and stay at the final potential for one day each.

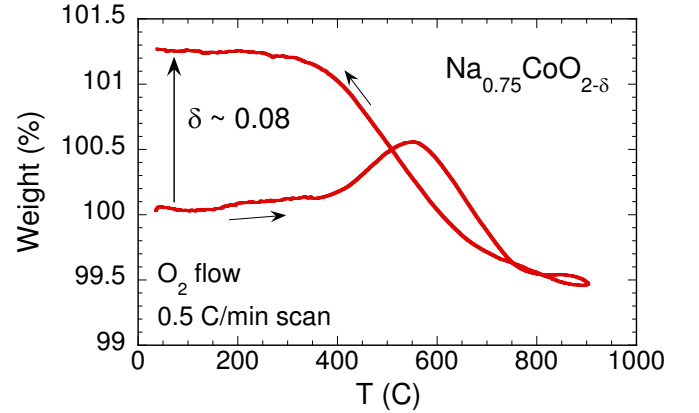
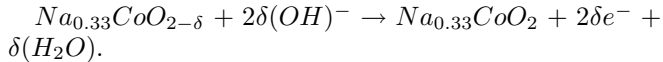


FIG. 5: (color online) The weight versus temperature of a powder sample with  $x = 0.75$ , which was quenched from  $900\text{C}$  to room temperature in the air.

to the Co ions. It is therefore likely that  $\text{Na}_x\text{CoO}_2$  is also prone to be oxygen deficient, especially for  $x$  below  $\sim 0.5$ . This may prevent the valence of the Co ions to be raised much beyond  $\text{Co}^{3.5}$ . In fact,  $\text{Na}_{0.7}\text{CoO}_{2-\delta}$  prepared with an oxygen partial pressure of  $\sim 0.2\text{ atm}$  has been reported to have an oxygen defect level as high as  $0.073$ .<sup>12</sup> By performing TGA measurements in an  $\text{O}_2$  environment, we find that powder samples of  $\text{Na}_{0.75}\text{CoO}_{2-\delta}$  (prepared at  $900\text{C}$  and quenched in air) have a value of  $\delta$  very close to  $\sim 0.08$ , as shown in Fig. 5. In contrast, we find that a FZ crystal of  $\text{Na}_{0.75}\text{CoO}_2$  (quenched from high temperature in an oxygen atmosphere) does not pick up oxygen under the same annealing process. Hence, for the as-grown single crystals with  $x = 0.75$ , the oxygen deficiency level is small ( $\delta \sim 0$ ).

For the powder samples of  $\text{Na}_{0.75}\text{CoO}_{1.92}$ , the oxygen non-stoichiometry remains even after the electrochemical de-intercalation process. Such a sample was used in the

potential step experiment shown in Fig. 3. To reduce the Na content from 0.75 to 0.33, a total charge of 0.42 e<sup>-</sup>/f.u. is required, which is indicated by the position of steepest slope near  $\sim 0.42$  e<sup>-</sup>/f.u. as shown in the figure. If the oxygen deficiencies are being compensated, then an additional charge equal to 0.16 e<sup>-</sup>/f.u. would be required through the reaction



The fact that no additional charge is observed during the electrochemical charging suggests that the oxygen deficient state,  $\text{Na}_{0.33}\text{CoO}_{1.92}$ , is the final equilibrated phase. We find that upon cooling  $\text{Na}_{0.33}\text{CoO}_{1.92}$  from 900C in  $\text{O}_2$ , the sample does not pick up additional oxygen to yield  $\text{Na}_{0.3}\text{CoO}_2$ , in contrast to the  $x = 0.75$  compound. By means of titration experiments, Karppinen *et al.* have shown that the Co valence of fully hydrated, partially dehydrated, and non-hydrated  $\text{Na}_{0.36}\text{CoO}_2$  is essentially identical in all three compounds with a value of +3.48.<sup>19</sup> Hence, it appears that the oxygen deficiency level of  $\delta \sim 0.08$  keeps the Co valence state near +3.5, even for Na contents significantly less than  $x = 0.5$ .

### III. DISCUSSION AND CONCLUSIONS

The various stable phases that we have observed upon electrochemical de-intercalation may be related to preferred Na concentrations for the formation of ordered Na superlattices. Various types of Na superstructures in  $\text{Na}_x\text{CoO}_2$  have been identified in both experimental and theoretical work.<sup>20,21,22,23</sup> For a structure with hexagonal symmetry, the systematic loss of one out of six Na ions from the lattice naturally describes a series of samples with  $x$  near  $5/6=0.83$ ,  $4/6=0.67$ ,  $3/6=0.5$  and  $2/6=0.33$ . However, stable phases with  $x \sim 0.44$ ,  $0.61$ ,  $0.625$ ,  $0.72$  and  $0.75$  have also been observed via phase boundaries studies of solid state reactions, or by electrochemical de-intercalation/interaction sweeps.<sup>24,25</sup> We note that phases with  $x$  equal to an integer multiple of  $1/6$  or  $1/8$  can easily be constructed out of a systemic loss of Na from a hexagonal basic unit cell (3 Na per unit) or a rectangular unit cell of  $2\sqrt{3}a \times 2a$  (8 Na per unit). Starting with fully filled Na-II sites ( $2/3, 1/3, 1/4$ ) with  $P6_3/mmc$  symmetry, the existence of stable phases near  $x = 1/3 = 0.33$  and  $x = 2/3 = 0.67$  are naturally obtained through systematic loss of Na from the hexagonal unit. On the other hand,  $x = 2/8 = 0.25$ ,  $x = 4/8 = 0.5$ ,  $x = 5/8 = 0.625$  and  $x = 6/8 = 0.75$  can be constructed through the systematic loss of Na from the  $2\sqrt{3}a \times 2a$  unit. Most of these proposed superstructures have not been observed with diffraction methods. It appears likely that only the  $x = 0.5$  composition has long-range Na order (as reported by Huang *et al.*<sup>22</sup>).

Our results have also shown that the phases with  $x = 0.5$  and  $0.3$  have very similar chemical potentials for

Na in the lattice. In prior work<sup>17</sup>, we have observed weak magnetic susceptibility anomalies near 53K and 88K in some electrochemically prepared crystals with  $x = 0.3$ . This behavior of the susceptibility is similar to observed in  $\text{Na}_{0.5}\text{CoO}_2$  which is reported to have a low temperature charge- and spin- order state.<sup>10,26</sup> A possible scenario for the existence of 53K and 88K anomalies in a crystal with  $x = 0.3$  is that phase separation of Na occurs over long time scales. Our current observation of oxygen deficiency in samples with  $x < 0.5$  points toward another possibility. In this scenario, compounds with  $x = 0.5$  will have an average Co valence of +3.5 in the absence of oxygen depletion. If reducing the Na content simultaneously creates oxygen deficiencies, then the average Co valence can remain at +3.5, similar to the case of  $\text{Li}_x\text{CoO}_{2-\delta}$ .<sup>11</sup> Hence, the weak anomalies we observe in the susceptibility of  $\text{Na}_{0.3}\text{CoO}_{2-\delta}$  may arise from regions in the sample with significant oxygen deficiency such that the local average Co valence remains at +3.5.

In summary, we have presented results characterizing samples of  $\text{Na}_x\text{CoO}_2$  prepared by floating-zone crystal growth and electrochemical de-intercalation. We have found that the floating-zone method of crystal growth often yields crystals with significant amounts of CoO impurity inclusions. However, the impurity phase may be minimized by carefully choosing the feeding rate and pulling rate. During the de-intercalation process, a potential step method was employed to identify the stable phases of  $\text{Na}_x\text{CoO}_2$ . We find that the stable Na concentrations correspond to fractions which are close to multiples of  $1/6$  or  $1/8$ . This may indicate a tendency for the Na ions to form short-range ordered superstructures. Finally, we have observed that oxygen deficiencies (at a level as high as  $\delta \simeq 0.08$ ) may exist in  $\text{Na}_{0.75}\text{CoO}_{2-\delta}$  as well as de-intercalated  $\text{Na}_{0.3}\text{CoO}_{2-\delta}$ . The presence of oxygen deficiencies must certainly be taken into account when comparing experimental data on different samples of  $\text{Na}_x\text{CoO}_{2-\delta}$ .

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- \* On leave from Physics Department, Pusan National University, Korea.
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